09/869544

PCT/AU99/01140

4

REC'D 23 FEB 2000

WIPO PCT

AU99/1140

Patent Office
Canberra

I, KAY WARD, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PP 7988 for a patent by CERAMIC FUEL CELLS LIMITED filed on 31 December 1998.

COMMONWEALTH OF AUSTRALIA
AUSTRALIA
PATENT OFFICE

WITNESS my hand this
Sixteenth day of February 2000

K Ward

KAY WARD
TEAM LEADER EXAMINATION
SUPPORT AND SALES

PRIORITY DOCUMENT
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Regulation 3.2

Ceramic Fuel Cells Limited

A U S T R A L I A

Patents Act 1990

PROVISIONAL SPECIFICATION

for the invention entitled:

"Electrically Conductive Ceramics"

The invention is described in the following statement:

ELECTRICALLY CONDUCTIVE CERAMICS

The present invention relates to electrical conductivity in metal oxide ceramic materials and the creation of electrical conductivity in a normally non-conductive ceramic material. It has application in providing electrical conductivity across a layer of ceramic material. In a particular application the layer of metal oxide ceramic is adhered to a metal plate and this has special application in components of solid oxide fuel cells.

Alumina is well known as an electrical insulator and as a material which is physically and chemically stable at high temperatures. Its electrical properties are put to good use in many high temperature applications where electrical isolation is desired. However, it would be useful in many applications to have a material which has the high temperature stability of alumina and other metal oxide ceramics while also having good electrical conductivity. It would be particularly useful if thin layers or sheets of metal oxide ceramics could be made selectively electrically conductive through the sheet.

The noble metals, including silver, have been used to bond alumina components together, but electrical conduction was not the aim, nor has it been reported as an outcome.

It has now been found that the application of silver metal, in any of a variety of forms, to the surface of a fully dense or porous layer sheet film or thin plate (hereinafter for convenience referred to as "layer") metal oxide ceramic such as alumina or chromia, followed by a sustained heat treatment at temperatures in the range 750°C-970°C or above, can cause the ceramic to develop electrically conductivity, especially in the immediate vicinity of the silver. The conductivity so imparted to the alumina may be a volume effect, that is, the conductivity may be imparted both laterally and through the thickness of the layer, film or plate. However, with very small thicness, the effect may be principally through the layer, film or plates.

Thus according to a first aspect of the present invention there is provided a layer of metal oxide ceramic material rendered electrically conductive by the incorporation of silver into the layer.

Preferably the ceramic material is alumina. Preferably the layer of metal oxide ceramic material has a thickness of no more than 1 mm, more preferably no more than 10 μm.

According to a second aspect of the invention there is provided a method of making an electrically insulating layer of metal oxide ceramic material electrically conductive including placing a silver-containing material into contact with the ceramic material and heating the ceramic and silver-containing materials in contact with each other to a temperature of at least 750°C such that silver migrates from said silver-containing material into said layer of metal oxide ceramic material and creates electrically conductive pathways through the layer.

In a solid oxide fuel cell the electrolyte, anode and cathode are normally ceramic materials. However, the surrounding structural components of a fuel cell stack may be of any material which can provide the required electrical conduction properties and structural strength to the stack assembly, at the temperatures necessary for operation of the fuel cell, for example in excess of 800°C. These components may be made of a ceramic or metal capable of handling the conditions. Some of these components, for example bipolar plates (also known as interconnect plates), are required to provide electrical connection between adjacent fuel cells. Sophisticated electrically conductive ceramics have been developed for this purpose but these materials are expensive, mechanically fragile and are poor thermal conductors when compared with many metals capable of handling the conditions.

The operating conditions in a solid oxide fuel cell are very severe on most metals, causing them to degrade via loss of mechanical strength, oxidation or other form of corrosion, distortion, erosion and/or creep. Various heat resistant metals have been developed to cope with many of these forms of degradation. Most such metals are alloys based on iron or nickel with substantial additions of chromium, silicon and/or aluminium, plus, in some alloys, more

expensive elements such as cobalt, molybdenum and tungsten. Chromium based metals are also available.

The significant feature of all heat resistant steels is the oxide layer, particularly its type and nature, which they form when exposed to mildly and strongly oxidising conditions at elevated temperatures. They all form tight, adherent, dense oxide layers which prevent further oxidation of the underlying metal. These oxide layers are composed of chromium, aluminium or silicon oxides or some combination of these depending upon the composition of the sheet. They are very effective in providing a built-in resistance to degradation of the underlying steel from high temperature oxidation.

However, while this feature is used to great advantage in many applications, the presence of this oxide layer is highly deleterious to the use of these steels in key components of solid oxide fuel cells. These oxides, especially those of silicon and aluminium, are electrically insulating at all temperatures and this is a major problem for those fuel cell components which must act as electrical current connectors. For these heat resisting steels to be useful for electrical conducting components in fuel cells, it is imperative that the insulating effect of the oxide layer be alleviated.

According to a third aspect of the invention, there is provided a component formed of steel having a surface layer of alumina chromia or alumina-rich or chromia-rich ceramic, said layer having been rendered electrically conductive by the incorporation of silver into the layer.

The ceramic layer protects the underlying metal from chemical attack while its electrical conductivity allows it to provide electrical contact with the underlying metallic component.

According to a fourth aspect of the invention there is provided a method of manufacturing a steel component with a heat-resistant and electrically conductive surface layer, said method including selecting a steel which forms an alumina or chromia surface layer in oxidizing atmosphere, placing a silver-containing material in contact with the surface of the steel,

heating the steel and silver-containing material to at least 750°C in an oxidising atmosphere to cause an alumina, chromia or alumina-rich or chromia-rich layer to form on the steel and to cause silver from said silver-containing material to occur in said layer and to create electrically conductive pathways through said layer.

Preferably the blood has an aluminium content of above 4.5 wt % .

Preferably, the temperature is at least 800°C, more preferably at least 850°C, even more preferably at least 900°C and most preferably at least 950°C. It is believed that while the effect of the silver imparting electrical conductivity to the metal oxide ceramic material will occur at 750°C, or even less, the rate of the effect occurring is very slow at this temperature and increases with increasing temperature.

For fuel cell applications, an advantage of the present invention is that a material such as alumina which is universally renowned for its excellent thermal and electrically insulating properties and its chemical inertness can have one of these three properties reversed without impairing the other two. The treatment produces a material which is still an excellent refractory material and inert in nearly all environments, but is electrically conductive at least in selected portions. This is of special significance for various connections required in fuel cell assemblies. The effect has been found to be durable over long periods of time and the full temperature range required for solid oxide fuel cell operation. The invention has been used to advantage to convert otherwise highly insulating alumina coated metal bipolar plates to conducting plates which can be used to collect current from operating fuel cells. The conductivity can be used as a sole means of current collection or used as a safeguard/backstop in case a prime current collector mechanism fails.

The silver may be in sheet, mesh or other appropriate form and may be commercially pure or impure, for example alloyed. The silver may be provided on a substrate of a type which is acceptance to the end result. The mechanism by which the silver migrates or occurs in the metal oxide ceramic layer is not fully understood at this time.

Embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a diagrammatic representation of an experimental arrangement used to investigate the nature of the invention;

Figure 2 is a plot of results recorded from an experiment of the form shown in Figure 1;

Figure 3 is a plot of results recorded from a variant of the experiment shown in Figure1.

Referring to Figure 1, two coupons 2 and 3 of clean, polished chromia-rich stainless steel approximately 1.0 cm square and 1 mm thick had sandwiched between them a square piece of silver foil 5 having a plan area of 0.864 cm2. The sandwich structure was clamped together, as indicated by arrows 7, with a force of 6N. Seals 8 between the coupons around their edges were pliable at elevated temperature and took no significant load.

The facing surfaces 9 of the coupons 2 and 3 were maintained in an atmosphere of gently flowing dry air, facilitated by an array of straight parallel grooves machined into the facing surfaces 9. The complete assembly was heated to 900C and maintained there for over 70 hours. A constant DC electric current of about 200 mA/cm2 was maintained between the coupons 2 and 3 by means of a current generator 12 and the voltage across the coupons was measured by a meter 14. The material of seals 8 was an electrically insulating glass so the measured voltage indicated the change in resistance in the electrical path between the two coupons 2 and 3. The steel in the coupons had a composition of about 27% Cr, 0.05% C, 0.05% Al and 0.05% Si by weight so its heat resistance and chemical resistance properties derive from the formation of a thin chromia layer on the surface of the steel in the oxidising atmosphere.

By the time the first reading was taken after heating to 900°C, a thin chromia layer had developed on the surfaces 9.

As seen from Figure 2, the resistance then dropped from 2 milliohm to 0.3 milliohm over 70 hours operation, which was a period when it would have been expected that the resistance would increase due to thickening of the chromium oxide layer on the surfaces 9 of the coupons in contact with the foil. Removal and examination of the coupons revealed a chromia layer had been generated on the facing surfaces 9 but that the chromia was electrically conductive through its thickness where the silver had been in contact with it. It is believed that the silver penetrates the growing chromia layer and improves its conductivity. If the same experiment were performed with a stainless steel foil instead of the silver foil, the chromia layer produced on the surfaces 9 would provide a resistance in the range of thousands of ohms per square centimetre instead of the thousandths of ohms per square centimetre found using the silver foil.

In a further experiment using a similar apparatus, the coupons used were similar to those described above but of a stainless steel which produced an alumina protective coating when heated. These were heated at 1025C in air for 1 hour to produce a coating of tightly adhered alumina approximately 1 to 2 μm thick on the exposed surface. The alumina coating was electrically insulating, with a resistance in excess of 3000ohm/cm2 (measured to a clean polished surface at the rear face). The coupons were then assembled as shown in Figure 1, with silver mesh taking the place of foil 5, and held in air at 850°C. The mesh was made from silver wire about 50 μm diameter woven at about 120 μm centres. The results are shown on Figure 3. After 420 hours the resistance across the sandwich had dropped to about one third of its starting value and was continuing to reduce. The 1 to 2 μm thick tightly adherent layer of alumina had become electrically less resistive at the places where the silver mesh was in contact with it.

It has been found that is it not necessary for the foil or mesh used to be of solid silver. When an expanded metal mesh made from stainless steel and electrocoated with silver was substituted for the solid silver mesh described above, the resistance of the alumina layer reduced in the same manner. It therefore appears that only small quantities of silver are required to be transferred from the mesh to the alumina in order for the effect to occur.

Likewise, it is believed the silver may be alloyed.

In a further experiment of the general form shown in Figure 1, the coupons were again a self-aluminising stainless steel pre-treated at 1025°C for 1 hour as above to produce an alumina layer thereon and, instead of mesh pressed between the coupons, a small quantity of silver paste was substituted. The coupons were then exposed to an air atmosphere at approximately 950°C and the resistance was observed to drop at a much faster rate than with the silver mesh at 850°C.

In a further series of experiments the stainless steel was polished to remove any oxide coating and the silver paste was applied between the polished coupons before any heating. The coupons were then heated in air at temperatures from 800°C to 970°C. Although an alumina coating quickly established itself on the surface of the steel, its resistance remained less than 10milliohm/cm2. The coating remained conductive when the temperature was reduced to ambient and through many such heating and cooling cycles. The silver and silver paste is quite pervious to oxygen, so the alumina layer is not prevented from developing on the surface of the steel, but it does develop with a low electrical resistivity.

The behaviour of the chromia and alumina in the way described was surprising. The structure of the conductive chromia and alumina has not yet been properly determined, nor has the mechanism by which the silver produces the conductivity in the oxide. While not intending to be bound by any theory, it is thought that when heated, small amounts of the silver are drawn threadlike along grain boundaries in the oxide and create an open mesh arrangement of silver threads or strands within the alumina such that there is eventually created a continuous path of silver strand along the grain boundaries through the full thickness of the layer of oxide.

Much effort has been spent developing heat resistant steels for bipolar plates for solid oxide fuel cells. Self-aluminising steels (>4.5 wt% Al) have particular advantages at the high operating temperatures required. If the coated surface is damaged in some way, it becomes

self healing as aluminium in the steel diffuses to the exposed surface where it oxidises to form a new protective coating of alumina. The alumina coating also has the beneficial property of totally blocking any escape of chromium from the steel. This is important because even small traces of chromium in an atmosphere will quickly and permanently reduce the performance of a solid oxide fuel cell. However the great benefits of self-aluminising steels have often been forgone because of the need to have the surface of the plate function as an electrical current collector, and this has been incompatible with alumina's properties as an electrical insulator. Thus the emphasis has been to develop steels which do not produce an alumina-rich layer upon their surface when exposed to oxidising atmospheres at high temperatures. In contrast, the present invention means that the benefits of an alumina coating may be obtained without the disadvantage of its high electrical resistance.

In addition to bipolar plates, the invention may be used for other components of fuel cells, particularly solid oxide fuel cells, such as current collector straps and heat exchangers.

Fuel cell components, and bipolar plates in particular, made in accordance with the third aspect of the invention with an alumina or alumina-rich layer may be superior to those obtainable with other heat resistant materials currently available in one or more of the following properties:

Stronger and Tougher: At the operating temperature of the fuel cell and during the warm up and cool down phases.

Cost: The cost of fuel cell components in accordance with the invention is less than other materials which have been used for interconnect plates in solid oxide fuel cells, e.g. Ni alloys, austenitic stainless steels, chromium alloys and ceramics.

Oxidation Resistance: The components have an excellent, inherent resistance to surface degradation at temperatures within the range 500°C to 950°C in the atmospheres usually present in a solid oxide fuel cell, viz moist air, moist hydrogen, moist hydrocarbons and

carbon.

Electrical Conductivity: The alumina or alumina-rich layer is electrically conductive from its exposed surface through to the underlying metal, thus providing a pathway for electrical contact and current flow through the component.

It is probable that in addition to its use with fuel cells, the invention has advantages in many areas of technology where insulating and conducting elements are used in close proximity and/or stable electrical properties at elevated temperatures are required. Technologies such as thick and thin film printed circuit boards, microelectronics, semiconductors, wave guides and sensors could benefit from the invention. There are many potential uses for alumina or chromia which is electrically conductive either in total or in selected areas.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and scope.

DATED this 31st day of December 1998.

Ceramic Fuel Cells Limited
By Their Patent Attorneys
DAVIES COLLISON CAVE

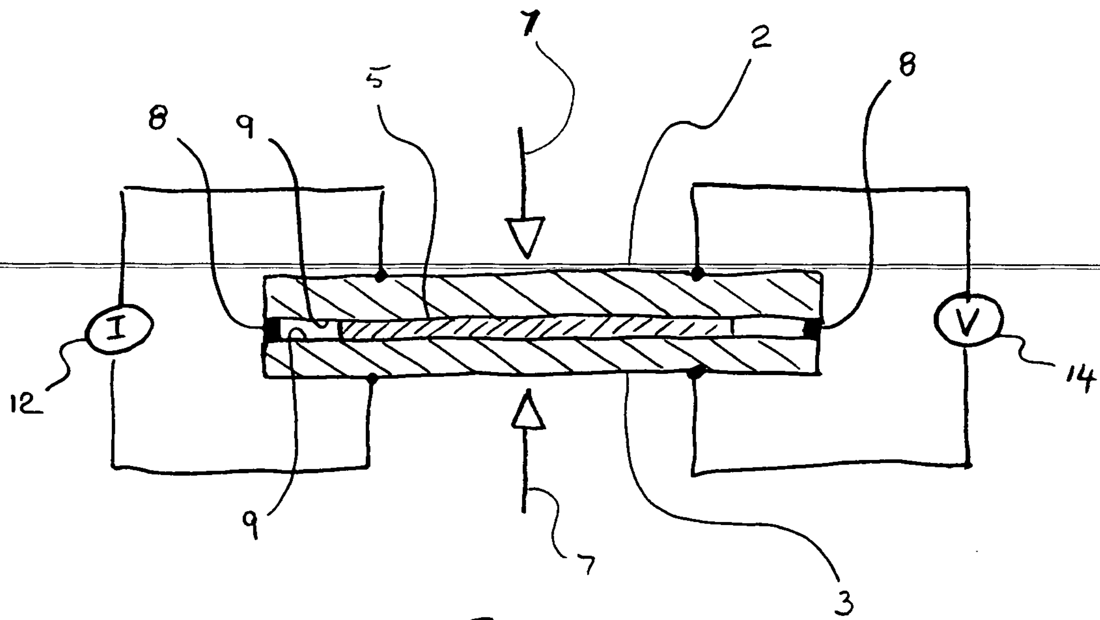

Fig. 1

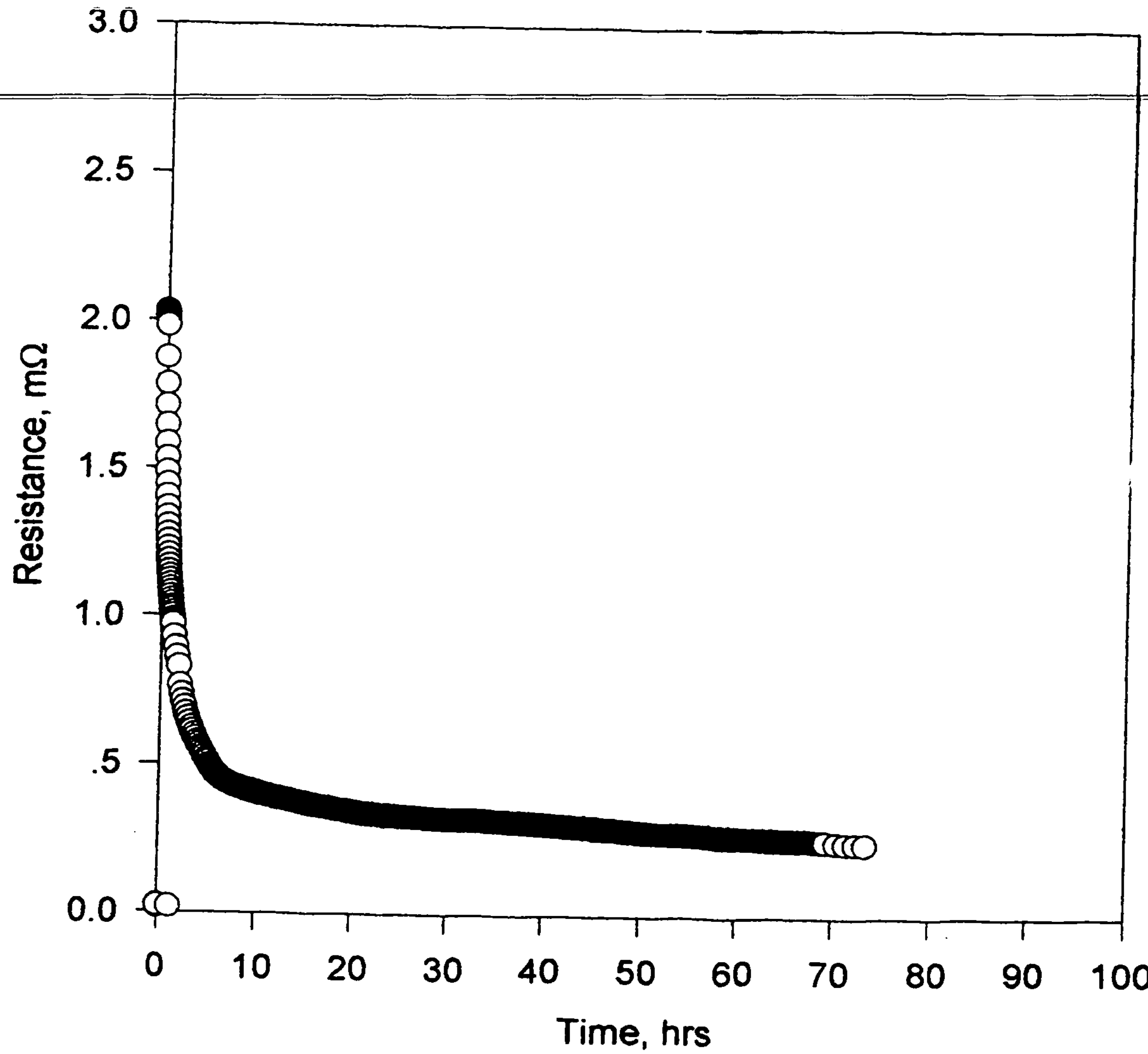
3.0
2.5
2.0
1.5
1.0
.5
0.0
Resistance, mΩ
0
10
20
30
40
50
60
70
80
90
100
Time, hrs

Fig. 2

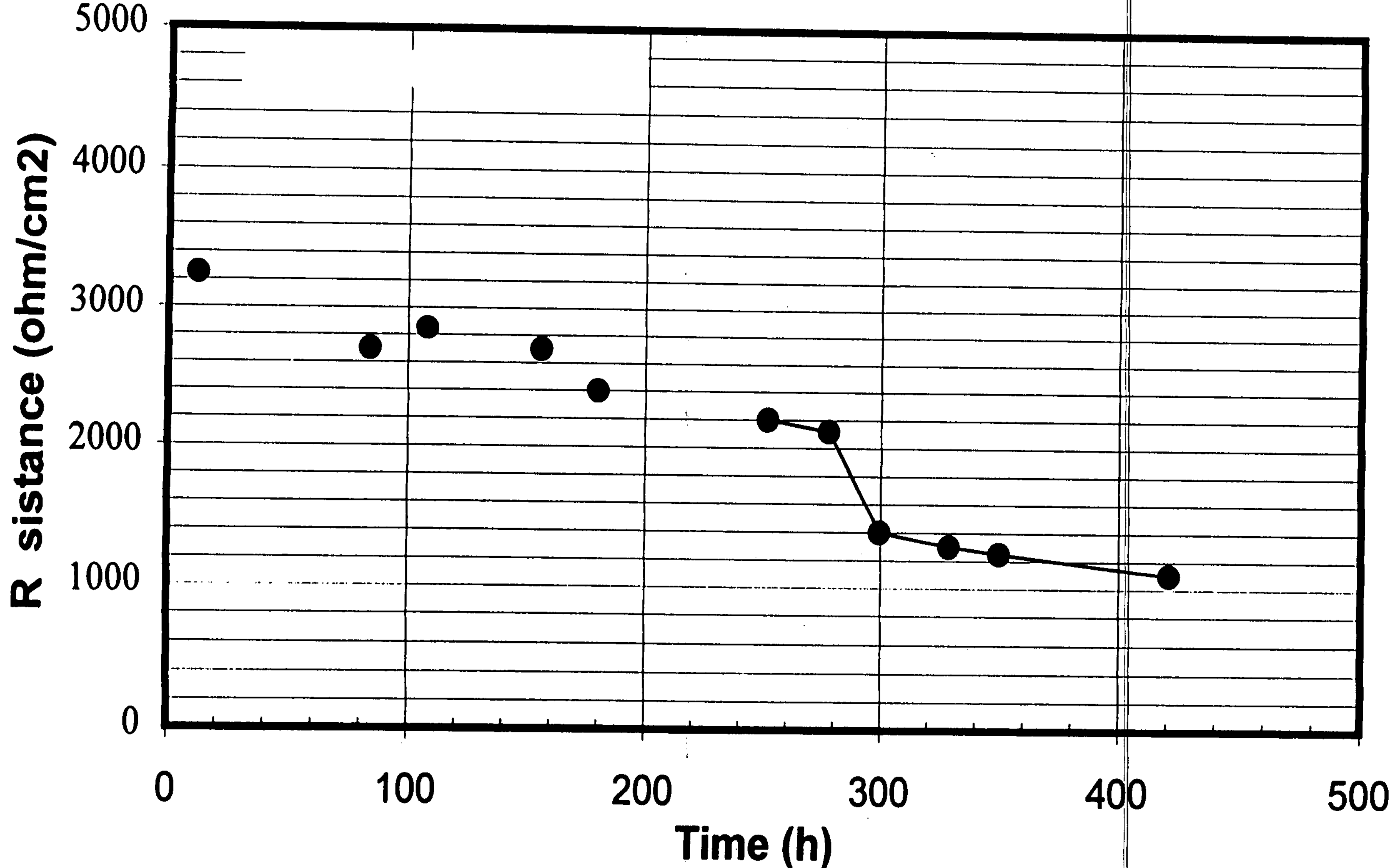
5000
4000
3000
2000
1000
0
R sistance (ohm/cm2)
0
100
200
300
400
500
Time (h)

Fig.3